

Europäisches
PatentamtEuropean
Patent OfficeOffice européen
des brevets

REC'D 03 APR 2003

WIPO PCT

Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

02075219.2

PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

BEST AVAILABLE COPY



Anmeldung Nr:
Application no.: 02075219.2
Demande no:

Anmeldetag:
Date of filing: 18.01.02
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

Nederlandse Organisatie Voor Toegepast-
Natuurwetenschappelijk Onderzoek Tno
Schoemakerstraat 97
2628 VK Delft
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Process for cleaning filters

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s)
revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

B01D/

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of
filing/Etats contractants désignés lors du dépôt:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR

Process for cleaning filters

(94)

[0001] The invention relates to a process of cleaning food processing equipment, in particular membrane filters which are used for producing foodstuffs or for cleaning water, wherein the filters are contacted with a cyclic nitroxyl compound and a reoxidator, or with a cyclic nitroxonium compound.

[0002] In the food industry, use is being made to an increasing extent of membrane filters, in particular plastic membranes such as polyvinylpyrrolidone, polysulphone, polyether-sulphone and certain types of polyamides, for removing undesirable insoluble matter from beverages and other liquids. Such membranes are also used for cleaning surface water. Such membranes ensure an expedient removal of undesirable constituents, in particular micro-organisms such as algae, fungi and bacteria.

[0003] The problem is, however, that such membrane filters become blocked even after a short time so that they become unusable. The blocked filters can be regenerated, for example by rinsing them through in the opposite direction. However, that is a complicated process and no longer effective in the long term because the contamination accumulates. In addition, it is difficult to remove some persistent organic contaminants in this way.

[0004] WO 97/45523 describes the use of 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) as nitroxyl compounds and hypochlorite and hypobromite as a reoxidator for cleaning beer-settling modules. The presence of halogen residues, especially bromine residues is highly undesired in equipment used for preparing or treating beverages and other foodstuffs. Also the effective life time of the filters and their tear strength are negatively affected by the presence of bromine compounds.

[0005] WO 99/15256 discloses the use of cyclic nitroxyl compounds such as TEMPO together with a calcium sequestering agent for cleaning filters to be used in purifying surface water.

[0006] The oxidation of carbohydrates and other primary alcohols with nitroxyl compounds and peracid, especially peracetic acid in the presence of catalytic amounts of bromine, is known as such from WO 99/57158.

[0007] It was found that filters and other equipment used in the food and beverage industry and in water purification can be effectively cleaned in a halogen-free process by applying a cyclic nitroxyl compound. The reoxidator of the nitroxyl compound can be a

peracid, or a hydroperoxide and/or a metal complex, e.g. in the form of an oxidative enzyme.

[0008] In the following description, cyclic nitroxyl compounds to be used in the present invention are exemplified by TEMPO only for the sake of simplicity, but it
5 should be understood that other di-tert-alkyl nitroxyls, such as 4,4-dimethyloxazolidine-N-oxyl (DOXYL), 2,2,5,5-tetramethylpyrrolidine-N-oxyl (PROXYL) and 4-hydroxy-
TEMPO and derivatives thereof and those described in WO 95/07303 can be substituted
for TEMPO. Especially preferred are TEMPO, 4-acetamido-TEMPO and 4-acetoxy-
TEMPO. The catalytic amount of nitroxyl is preferably 0.1-2.5% by weight, based on
10 the primary alcohol, or 0.1-2.5 mol% with respect to the primary alcohol.

[0009] The peracid may be any peralkanoic acid such as peracetic acid, perpropionic
acid, perlauric acid etc., a substituted alkanoic acid such as peroxytrifluoroacetic acid,
an optionally substituted aromatic peracid such as perbenzoic acid or m-chloro-
perbenzoic acid, or an inorganic peracid such as persulphuric acid or permanganic acid.
15 The peracids may be formed *in situ* from a precursor such as the corresponding
aldehyde, (carboxylic) acid, acid anhydride, ester or amide, e.g. tetra-acetyl-ethylene-
diamine (TAED), with a suitable halogen-free oxidising agent, such as hydrogen
peroxide or oxygen, either before the oxidation reaction or during the oxidation reaction,
or with perborates or percarbonates or the like, in the presence of acylating agents such
20 as TAED. The peracid reoxidises the spent nitroxyl *in situ* to produce a nitroxonium ion
which is the effective oxidator in the cleaning process of the invention. The peracid is
typically used in a concentration in the cleaning liquid of between 25 and 2500 ppm
(about 25 mg to 2.5 g per l). The peracids may be used as such, or in the form of a
suitable salt, especially an alkali metal salt. A suitable form of persulphuric acid is e.g.
25 Oxone® (2KHSO₅.KHSO₄.K₂SO₄), which is commercially available.

[0010] The reoxidation of the spent nitroxyl *in situ* can also be performed using a
hydroperoxide or a metal complex or preferably both, wherein the metal complex is an
intermediate oxidator. The metal complex may comprise e.g. vanadium, manganese, iron,
cobalt, nickel or copper with complexing agents, in particular polyamines, such as 2,2'-
30 bipyridyl, phenanthroline, tetramethyl-ethylenediamine, pentamethyldiethylenetriamine
and their cyclic counterparts such as 1,4,7-trimethyl-1,4,7-triazonane, and histidine and its
oligomers. The hydroperoxide may be hydrogen peroxide or an alkyl and ar(alk)yloxy-
hydroperoxide(such as tert-butyl hydroperoxide), wherein hydrogen peroxide is preferred.

[0011] It was found surprisingly that treatment of membrane filters and other equipment with TEMPO and a peracid such as persulphuric acid or a hydroperoxide results in a cleaning performance which is equal to or better than that of treatment with hypochlorite/bromide as described in WO 97/45523, and has the additional advantage that the membrane filter are not attacked by the cleaning agents to any detectable level, as assessed using with membrane strength measurements. Moreover, the absence of halogens is of a considerable advantage, for environmental reasons, but also as to the strength of the equipment treated, especially in the case of membranes.

[0012] The nitroxyl can also be oxidised in a separate reaction to form the nitroxonium ion *ex situ*. This can be effected using metal complexes as described above, such as copper/bipyridyl and oxygen or hydrogen peroxide, or with an oxidative enzyme such as laccase in the presence of oxygen. These processes are described in WO 00/50388 and WO 00/50621, which are incorporated herein by reference. This embodiment has the considerable advantage that the reoxidising agents, such as enzymes, metal complexes, hydrogen peroxide and the like do not come into contact with the filters or other equipment to be purified..

[0013] The process of the invention may be used for cleaning filters used in food industry and in feed industry, and equipment used in water purification. Such equipment may especially be used in the production of dairy products, beer, wine, fruit juices and other beverages and liquids used in food processing. Suitable examples of such equipment include pipes, tubes, capillaries, mixing devices and, in particular, filters. The filter may be of any type, including polymer membranes wherein the polymer may be polyvinylpyrrolidone, polysulphone, polyether-sulphone and certain types of poly-amides, and ceramic membranes made of e.g. silica, aluminium oxide etc.

The process of the invention may proceed by oxidation and/or solubilisation of carbohydrates and other high molecular weight primary alcohols such as proteinaceous materials, polyphenolic compounds, in residues to be removed from the filters. Such cleaning procedures are preferably carried out by treating the equipment with an aqueous solution of the nitroxyl compound and the peracid. The concentration of the nitroxyl compound can advantageously be in the range of 1 to 100 mg per l, especially 3 to 30 mg/l, and the concentration of the peracid can be in the range of 0.025 to 10 g per l, in particular 0.25 – 2.5 g/l. The process of the invention can be performed as a static process, i.e. batch-wise treatment of the equipment in a suitable container

containing the treatment liquid for a period of between several seconds and several hours, especially between 3 minutes and 1 hour. The process can also be a dynamic process, i.e. a process wherein a continuous or semi-continuous flow of the treatment liquid is passed over or through the equipment, e.g. at a rate of 5 ml to 10 l per minute, 5 depending on the size of the equipment. After the nitroxyl and peracid treatment, the equipment is rinsed with rinsing liquid, which can be water or a neutralising aqueous liquid or an organic solvent such as an alcohol solution, or a mixture or sequential combination thereof. Further details on the nitroxyl-catalysed treatment of filters and other equipment in the food industry can be found in WO 97/45523, which is 10 incorporated herein by reference. WO 99/15256, incorporated herein by reference, gives further details on the nitroxyl-catalysed treatment of filters in water purification.

Example 1: Cleaning filters using hypochlorite/TEMPO

A filtration membrane (hollow tube containing 40 membrane hollow fibers (pore size 0.5 micron) with a total surface area of 0.04 m² (resembling the X-flow R-100 modules 15 used in large scale facilities) was used for filtering beer. The membranes were fouled using a dead-end filtration technique until the pores were blocked resulting in minimal permeate or flux.

A solution containing 1000 ppm of hypochlorite and 35 ppm of TEMPO for half an hour was used to clean the membranes. The reaction pH was adjusted to 10. The cold 20 water flux (cwf) of the virgin membrane was 6000 l/h/m². The cwf after cleaning was also 6000 l/h/m².

Example 2: Cleaning filters using hypochlorite/bromide/TEMPO

A solution containing 1000 ppm of hypochlorite, 60 ppm bromide, and 35 ppm of TEMPO for half an hour was used to clean the membranes fouled according to Example 25 1. The reaction pH was adjusted to 10. The cold water flux (cwf) of the virgin membrane was 6000 l/h/m². The cwf after cleaning was also 6000 l/h/m².

Example 3: Cleaning filters using peroxosulphuric acid/TEMPO

A solution containing 1000 ppm of peroxosulphuric acid and 35 ppm of TEMPO for half an hour was used to clean the membranes fouled according to Example 1. The 30 reaction pH was adjusted to 8. The cold water flux (cwf) of the virgin membrane was 6000 l/h/m². The cwf after cleaning was also 6000 l/h/m².

Example 4: Cleaning filters using a manganese complex/hydrogen peroxide/TEMPO

Membranes as foul according to Example 1 were cleaned. The cleaning sequence started with a pretreatment of flushing the membranes with 0.5 M sodium hydroxide solution for 10 minutes followed a solution containing 2000 ppm of hydrogen peroxide (or 2000 ppm peracetic acid), 100 ppm of TEMPO, and 50 ppm of an Mn complex with 1,4,7-trimethyl-1,4,7-triazonane for half an hour was used to clean the membranes. The reaction pH was adjusted to 10. The cold water flux (cwf) of the virginal membrane was 6000 l/h/m². The cwf after cleaning was also 6000 l/h/m².

Example 5: Membrane stability data**10 (a) Stability in water:**

Six membranes (type MF05 M2 1.5 mm) derived from a virginal membrane module (type RX 300) were placed in a vessel containing water at ambient temperature for two months. At the end of the experiment the force needed to break the membranes was measured with a material tester from Stable Micro Systems type TA-HD equiped with a 15 50 N cell. The results are presented in table 1.

Table 1. Maximum force needed to break the membrane

Membrane	Max. force for breaking (N)
1	9.31
2	9.12
3	9.82
4	9.77
5	9.21
6	8.88

Mean 9.35 N

Standard deviation 0.37

20

(b) Influence of sodium hypochlorite:

Seven membranes (type MF05 M2 1.5 mm) derived from a virginal membrane module (type RX 300) were placed in a vessel containing a cleaning solution (35 ppm TEMPO, 1000 ppm sodium hypochlorite at pH 10 and ambient temperature). The cleaning 25 solution was refreshed every week during 2 months. At the end of the experiment the force needed to break the membranes was measured with a material tester from Stable Micro Systems type TA-HD equiped with a 50 N cell. The results are presented in table 2.

Table 2. The maximum force needed to break the membranes

Membrane	Max. force for breaking (N)
1	4.98
2	6.40
3	4.85
4	6.49
5	5.80
6	5.16
7	5.96

Mean 5.66 N

Standard deviation 0.673

5 **(c) Influence of sodium hypochlorite/sodium bromide:**

Eight membranes (type MF05 M2 1.5 mm) derived from a virginal membrane module (type RX 300) were placed in a vessel containing a cleaning solution (35 ppm TEMPO, 1000 ppm sodium hypochlorite and 60 ppm sodium bromide at pH 10 and ambient temperature). The cleaning solution was refreshed every week during 2 months. At the 10 end of the experiment the force needed to break the membranes was measured with a material tester from Stable Micro Systems type TA-HD equipped with a 50 N cell. The results are presented in table 3.

Table 3. The maximum force needed to break the membranes

Membrane	Max. force for breaking (N)
1	5.03
2	5.98
3	6.03
4	4.24
5	5.83
6	6.55
7	3.36
8	4.58

15 Mean 5.20 N

Standard deviation 1.085

(d) Influence of peroxosulphuric acid:

Six membranes (type MF05 M2 1.5 mm) derived from a virginal membrane module

20 (type RX 300) were placed in a vessel containing a cleaning solution (35 ppm TEMPO,

1000 ppm peroxosulphuric at pH 8 at ambient temperature). The cleaning solution was refreshed every week during 2 months. At the end of the experiment the force needed to break the membranes was measured with a material tester from Stable Micro Systems type TA-HD equipped with a 50 N cell. The results are presented in table 4.

5

Table 4. The maximum force needed to break the membranes

Membrane	Max. force for breaking (N)
1	9.50
2	8.79
3	9.33
4	8.60
5	9.47
6	8.48

Mean 9.03 N

Standard deviation 0.46

10 It is to be concluded that the membranes are susceptible to breakage when oxidants like hypochlorite/bromide (hypohalites) are used in combination with TEMPO as a cleaning agent. The standard deviation in the forces needed to break the membranes increases significantly due to the addition of bromide to the hypochlorite/TEMPO cleaning solution. Therefore the chance of breakage of the membranes during a full 15 scale filtration (for instance beer) is significant higher when bromide is added to the cleaning solution (TEMPO/hypochlorite).

20 Furthermore the use of peroxosulphuric acid in combination with TEMPO seems to have a very minor effect only on the membranes in terms of breakage. The use of peroxosulphuric acid in combination with TEMPO as a cleaning agent is more favourable than hypohalites/TEMPO due to the fact that no halides are present in the waste. Another important advantage of peroxosulphuric acid is that corrosion of the filtration equipment does not occur compared to the hypohalite formulations.

Claims

1. A halogen-free process for cleaning food processing equipment, comprising contacting the equipment with a cyclic nitroxyl and a peracid or hydroperoxide reoxidator, or with a nitroxonium compound.
2. A process according to claim 1, wherein the reoxidator is a peracid or a salt thereof.
3. A process according to claim 2, wherein the peracid is peracetic acid.
4. A process according to claim 2, wherein the peracid is persulphuric acid.
5. A process according to any one of claims 2-4, wherein the peracid is produced in situ from hydrogen peroxide or from compounds releasing hydrogen peroxide.
6. A process according to any one of claims 2-4, wherein the peroxide is hydrogen peroxide in the presence of a metal complex or an oxidative enzyme.
7. A process according to any one of claims 2-6, wherein the reoxidator is used in an aqueous solution in a concentration of 25-2500 ppm.
8. A process according to any one of claims 1-7, wherein the cyclic nitroxyl compound is 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) or a 4-hydroxy-, 4-acyloxy- or 4-acylamino derivative thereof.
9. A process according to claim 1, wherein the nitroxonium compound has been prepared previously using a metal complex or an oxidative enzyme.
10. A process according to any one of claims 1-9, wherein the filter is a membrane filter.

EPO - DG 1

18.01.2002

(94)

Abstract

Filters used in the food and beverage industry can be cleaned by contacting the filters with a cyclic nitroxyl compound and a reoxidator or with a nitroxonium compound in a bromine-free process. The nitroxyl can be TEMPO or its 4-acetamido or 4-acetoxy derivative, and the nitroxonium compound can be the corresponding oxidised ion obtained by enzymatic or metal catalysed oxidation. The reoxidator may be a peracid., such as peracetic acid, persulphuric acid or permanganic acid, or a metal complex with a hydroperoxide.

EPO - DG 1

18. 01. 2002

94

INTERNATIONAL SEARCH REPORT

PCT/NL 00039

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C11D11/00 C11D3/28 C11D7/32 C11D3/39 C11D7/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 195 03 060 A (HENKEL ECOLAB & CO OGH) 8 August 1996 (1996-08-08) claims 1,7 ---	1-10
A	US 6 274 186 B1 (MOL ET AL) 14 August 2001 (2001-08-14) cited in the application column 3, line 3 - line 13 claims 1-5 ---	1-10
A	WO 99 15256 A (BESEMER ET AL) 1 April 1999 (1999-04-01) cited in the application claims 1-3 ---	1-10 -/-

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the International filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the International filing date but later than the priority date claimed

T later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the Invention

X document of particular relevance; the claimed Invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed Invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the International search

1 April 2003

Date of mailing of the International search report

15/04/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Rasmusson, R

INTERNATIONAL SEARCH REPORT

PCT/NL 03/00039

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 00 50388 A (BESEMER ET AL) 31 August 2000 (2000-08-31) cited in the application page 1, line 9 - line 12 claims 1-6 -----	1-10

INTERNATIONAL SEARCH REPORT

PCT/NL 00039

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
DE 19503060		A	08-08-1996	DE AT DE DK WO EP	19503060 A1 178500 T 59601608 D1 808212 T3 9623579 A1 0808212 A1	08-08-1996 15-04-1999 12-05-1999 18-10-1999 08-08-1996 26-11-1997
US 6274186		B1	14-08-2001	NL AT AU AU BG BR CN CZ DE EP EP HU IL JP KR WO NO NZ SK TR	1003225 C2 228560 T 717265 B2 2915597 A 102972 A 9709282 A 1226922 A 9803922 A3 69717451 D1 1260576 A2 0912701 A1 9904021 A2 127318 A 2000511218 T 2000016193 A 9745523 A1 985602 A 333071 A 165798 A3 9802544 T2	03-12-1997 15-12-2002 23-03-2000 05-01-1998 30-09-1999 11-01-2000 25-08-1999 11-08-1999 09-01-2003 27-11-2002 06-05-1999 28-03-2000 20-05-2001 29-08-2000 25-03-2000 04-12-1997 18-01-1999 29-07-1999 13-03-2000 22-03-1999
WO 9915256		A	01-04-1999	NL AU WO	1007086 C2 9190198 A 9915256 A1	22-03-1999 12-04-1999 01-04-1999
WO 0050388		A	31-08-2000	AU AU BR BR CA CZ EP EP HU HU JP WO WO	2832800 A 2832900 A 0008474 A 0008478 A 2362717 A1 20013042 A3 1177308 A2 1173409 A1 0105299 A2 0200203 A2 2002537374 A 0050621 A2 0050388 A1 513649 A	14-09-2000 14-09-2000 22-01-2002 22-01-2002 31-08-2000 13-02-2002 06-02-2002 23-01-2002 29-04-2002 29-05-2002 05-11-2002 31-08-2000 31-08-2000 28-09-2001

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.